ELECTRICAL AND MAGNETIC PROPERTIES OF OXIDE-BASED DILUTED MAGNETIC SEMICONDUCTOR THROUGH RARE-EARTH DOPING

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ABSTRACT

In recent years, the ability of gadolinium-doped zinc oxide (Gd-doped ZnO) semiconductors to achieve ferromagnetism thin films at room temperature have attracted enormous attention among researchers and scientist due to their potential ideal materials for many applications such as solar cells, sensors, spintronic and etc. A necessary condition to realize towards new-functional devices is to have materials that exhibit ferromagnetism above room temperature. Diluted magnetic semiconductors (DMS) system is where the magnetic ions such as the transition metals and rare earth elements partially substitute the main group cation in wurzite structure. Ever since the discovery of the ferromagnetism in (In, Mn)As and (Ga, Mn)As, researchers have widely studied over other magnetic materials that has potential application towards new-functional devices. Gd rare-earth (RE) atoms have interesting magnetic properties which would induce ferromagnetism behavior with its small amount of doping concentration into ZnO compared to doping ZnO with the transition metals. However, systematic study on this new type of DMS is still lacking in terms of synthesis and materials properties in which room for improvement are still wide open in pursuing the suitable material for spintronic device. Therefore, in this research, Gd-doped ZnO thin films have been synthesized using sol-gel spin-coating technique. Series of experiments have been conducted to investigate the effect of several parameters such as different pre-annealing, post-annealing and hour annealing temperature, Gd contents (i.e. undoped to 16%) and varying the type of substrates (i.e. glass, aluminium (Al) doped ZnO (AZO), fluorine doped tin oxide (FTO) and silicon (Si)). As a result, the Gd-doped ZnO film with 4% of Gd content exhibits interesting magnetic behavior at room temperature. The properties of Gd-doped ZnO have been investigated using x-ray diffraction (XRD), field-emission scanning electron microscope (FESEM),

atomic force microscopy (AFM), ultra-violet visible spectrophotometer (UV-Vis), photoluminescence (PL), magnetic force microscopy (MFM) and vibrating sample magnetometer (VSM). The XRD analysis shows that the Gd-doped ZnO film is hexagonal wurzite structure and exhibits preferential growth along the (0 0 2) plane. The AFM image shows the surface of the film is homogeneous and uniform. In addition, the UV-Vis analysis indicates the film is highly transparent with average transmission of approximately 90% in the visible region. The MFM images show presence of magnetic domain on the film surface and VSM further confirmed the film is indicating magnetic properties at room temperature. For the four-point probe measurement, it shows that the electrical resistivity of sample on glass substrate is 2.01 x 10^2 Ω cm and the conductivity is 4.98 x 10^{-3} S/m. Meanwhile, sample on Si substrate shows higher conductivity of 9.9 S/m and lower resistivity of 1.01 x 10^{-1}. With this result, it shows that Si substrate is more compatible on fabricating devices.

ABSTRAK

Sejak kebelakangan ini, gadolinium (Gd)-didopkan zink oksida (ZnO) untuk membentuk filem nipis yang mengandungi feromagnet pada suhu bilik telah menarik perhatian di kalangan penyelidik dan ahli sains kerana potensinya sebagai satu bahan yang ideal untuk digunakan pada pelbagai aplikasi seperti aplikasi pengesan (sensor), *solar cells*, *spintronic* dan sebagainya. Di antara syarat-syarat yang diperlukan untuk merealisasikan ke arah peranti baru adalah dengan mempunyai bahan-bahan yang mempunyai tindak-balas feromagnet di atas suhu bilik. Sistem *diluted magnetic semiconductor* (DMS) adalah merupakan proses di mana berlaku peralihan ion logam ke dalam *wurzite structure*. Penemuan pertama kepada sifat feromagnet ini di dalam bahan seperti (In, Mn)As and (Ga, Mn)As, telah menyebabkan ramai penyelidik mengkaji dengan lebih meluas ke atas bahan-bahan magnet yang lain yang mana yang berpotensi ke arah peranti baru. Bahan nadir bumi iaitu Gd mempunyai sifat-sifat magnet yang unik yang boleh menghasilkan tindak-balas feromagnet yang kuat apabila didopkan dengan ZnO berbanding ZnO didopkan dengan bahan lain. Walau bagaimanapun, penyelidikan ke atas bahan ini masih lagi tidak mencukupi, terutamanya mengenai sifat feromagnet bahan tersebut. Dalam kajian ini, filem Gd-didopkan ZnO telah disintesiskan dengan menggunakan teknik *sol-gel* putaran-salutan. Pelbagai *parameter* pemprosesan telah dioptimakan seperti berbeza proses pra-penyepuhlindapan, berbeza proses selepas penyepuhlindapan dan berbeza masa untuk proses penyepuhlindapan, mengubah kandungan Gd (dari undop hingga 16%) dan berbeza jenis substrat (iaitu kaca, aluminium (Al) didopkan ZnO (AZO), fluorin oksidadidopkan tin (FTO) dan silicon (Si)). Oleh itu, 4% kandungan Gd telah menunjukkan sifat *ferromagnetism* pada keadaan suhu bilik berbanding kandungan Gd yang lain. Sifat-sifat ini, telah dikaji dengan lebih terperinci dengan menggunakan *x*-

ray diffraction (XRD), *field-emission scanning electron microscope* (FESEM), *satomic force microscopy* (AFM), *ultra-violet visible spectrophotometer* (UV-Vis), *photoluminescence* (PL), *magnetic force microscopy* (MFM) dan *vibrating sample magnetometer* (VSM). Analisis XRD menunjukkan bahawa filem Gd-didopkan ZnO adalah berstruktur *wurzite* heksagon dan mempamerkan orientasi pertumbuhan pada puncak yang utama iaitu (0 0 2). Imej AFM menunjukkan permukaan filem adalah homogen dan seragam. Di samping itu, analisis UV-Vis menunjukkan bahawa filem ini adalah lutsinar dan telus dengan isyarat penghantaran pada kadar purata 90% dalam kawasan yang boleh dilihat dengan mata kasar. Imej MFM menunjukkan kehadiran domain *magnet* pada filem dan dengan menggunakan VSM, ini dapat mengesahkan bahawa file mini adalah feromagnet pada kadar suhu bilik. Untuk pengukuran kerintangan elektrik, *four-point probe* telah digunakan dan keputusan mendapati bahawa kerintangan elektrik file mini adalah 2.01 x 10^2 Ω cm dan kekonduksian filem adalah 4.98 x 10 S/m. Manakala, sampel di atas filem Si menunjukkan konduktivit yang tinggi iaitu 9.9 S/m dan kerintangan elektrik adalah rendah iaitu 1.01 x 10^{-1}. Keputusan ini menunjukkan bahawa, filem Si adalah sangat sesuai dalam menghasilkan peranti-peranti elektronik.

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APPROVAL

I certify that an Examination Committee has met on **11 January 2017** to conduct the final examination of **Nurul Fadzilah binti Ab Rasid** on her degree thesis entitled **'Electrical and Magnetic Properties of Oxide-based Diluted Magnetic Semiconductor through Rare-Earth Doping'**. The committee recommends that the student be awarded the Degree of Master of Science (Electrical and Electronic Engineering).

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LIST OF ABBREVIATIONS AND SYMBOLS

ρ	-	Resistivity
σ	-	Conductivity
Wt%	-	Weight percentage
T_c	-	Curie temperature
DMS	-	Diluted Magnetic Semiconductor
TM	-	Transition metal
RE	-	Rare-earth
RT	-	Room temperature
FM	-	Ferromagnetism
Gd	-	Gadolinium
ZnO	-	Zinc oxide
Al	-	Aluminium
FTO	-	Fluorine-doped tin oxide
Si	-	Silicon
GaN	-	Gallium Nitrate
Mn	-	Manganese
FESEM	-	Field-emission scanning electron microscope
AFM	-	Atomic force microscopy
MFM	-	Magnetic force microscopy
UV-Vis-		Ultra-violet Visible spectrophotometer
PL	-	Photoluminescence Spectroscopy
VSM	-	Vibrating sample magnetometer
XRD	-	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Research Overview

Currently, nanotechnology is very popular among scientists and researchers around the world. It is one of the most important future technology because it concerns with the materials and structures for exhibiting the novelty. In the world of nanoscience and nanotechnology field, diluted magnetic semiconductor (DMS) is popular amongst the researchers and scientist around the world. It has been categorized into two parts with promising properties of both semiconductors; for logic computation and a new type of material which was formed by doping conventional semiconductors with transition element [1]. Diluted magnetic semiconductors system is where the transition metal ions partially substitute the main group cation in wurzite structure; transition metal (TM) and rare-earth (RE) [2]. There are two important factors in DMS which is Curie temperature (T_c) and the ferromagnetism in DMS material. Material such as manganese-doped gallium arsenide (GaAS:Mn) and manganese-doped indium arsenide (InAs:Mn) contain carrier-mediated ferromagnetism, but, these materials show that the T_c is far below from room temperature (RT) [1]. T_c is the most important magnetic properties for device applications. Figure 1.1 illustrates the process of how DMS is produced.

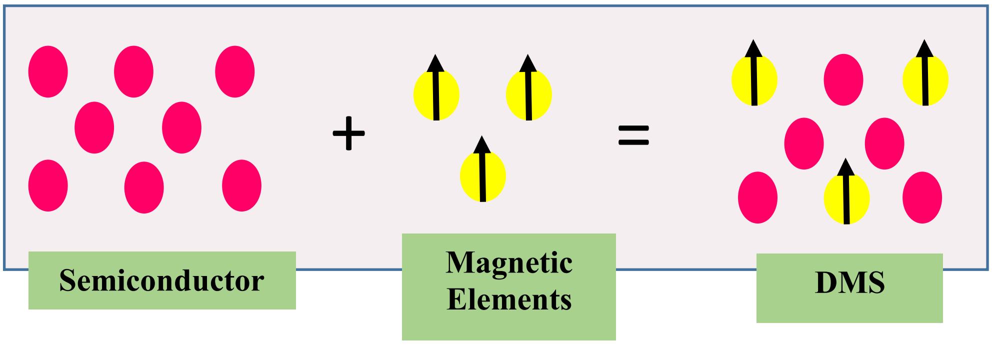

Figure 1.1 The illustration of DMS production

Mass, charge and spin of electrons are important in DMS; however, most applications are separated into two groups which are semiconductors and magnetic elements. When small amount of magnetic element is doped into a semiconductor, the DMS material is produced. This concept is likely similar to doping process. The observation of doping process has prompted a lot of interest in the field of spin-based-electronics (Spintronics) [3], which can be used to achieve new functionalities in electronic devices [4]. In order to control the spin state of carrier, DMS material should allow the injection of spin-polarization into the magnetic semiconductors [2-3]. The capability of controlling the spin and charge in electronic devices can improve efficiency [5-6], possibility of quantum computing and etc. Ferum (Fe), nikel (Ni), cobalt (Co), Manganese (Mn), vanadium (V) and chromium (Cr)[7] have been utilized to produce ferromagnetic compounds that possess interesting magnetic properties and applications [5,8].

Generally, previous studies [8-9] have found that the Mn is an ideal candidate as a magnetic dopants. The presence of Mn has shown to overwhelm the interaction between charge carriers. They discovered that Mn-doped InAs and Mn-doped GaAs was ferromagnetic with T_c of ~100 K [10]. The material was grown by using low temperature metal beam epitaxy (MBE) growth [3] in a temperature range of 200-

300°C to avoid the formation of secondary phases such as MnAs. The ferromagnetic behavior was observed in p-type samples below the *Tc*. The theoretical studies by Dietl *et al.* predicted that gallium nitrite (GaN) and zinc oxide (ZnO) should have T_c greater than room temperature because of their smaller lattice constant that are allowed the interaction between spins and holes which in turn lead to larger ferromagnetic coupling [11]. Besides that, ZnO has been suggested as a promising candidate as a host material for the magnetic element because ZnO itself is a diluted magnetic material with T_c above room temperature [10]. This prediction sparked amount of attentions to transition metal doped ZnO and other metal oxide-based DMS such as titanium oxide (TiO_2) and tin oxide (SnO_2) [12].

1.2 Problem statement

The rapid growth interesting in nanotechnology has led to the development of realizing new-functional devices such as spintronic. One of the means to address this issue is the materials to fabricate the films for developing the devices. Many researchers has studies and developed various types of material from transition metals to rare-earth metals element. However, generating reproducible magnetic behavior in wide bandgap DMS materials remains a major obstacle to the fabrication of spintronic devices above room temperature [5]. This obstacle has prompted significant research on ZnO and rare-earth dopants have emerged as promising candidates in ZnO and have been the subject of intense investigations. Recently, most of the effort was focused on improving materials for spintronic applications using various kind of method [7]. Therefore, the investigation on the structural, optical, magnetic and electrical properties of Gd-doped ZnO is carried out in this study for these applications using an easy and simple method that does not required high vacuum. With this easy and simple method, Gd-doped ZnO properties can also be improved and achieve magnetic behavior above room temperature.

1.3 Hypothesis

The manipulation of Gd-doped ZnO by using spin-coating sol gel method parameters such as pre-annealing temperature, annealing temperature, different Gd concentrations and different substrates will result in changes of morphological, structural, electrical, optical and magnetic properties. From the results, the optimum condition for n-type Gd-doped ZnO thin film with interesting magnetic behavior can be produced.

1.4 Objective

The main purpose of this study is to achieve the following objectives:

i. To investigate the effect of Gd dopants into ZnO thin films.
ii. To determine the room temperature ferromagnetism of Gd-doped ZnO thin films.
iii. To assess the influence of different substrates on the structural, magnetic and electrical properties of Gd-doped ZnO films.

1.5 Scopes

The scopes of this research are:

i. Deposition of Gd-doped ZnO thin films onto different types of substrates (glass and silicon) using sol-gel spin coating technique.

ii. Optimization of growth parameters; different pre-annealing and annealing temperature, different time of annealing process and different Gd contents with or without seed layer.

iii. Characterization of the structural, optical, magnetic and electrical properties of Gd-doped ZnO films.

1.6 Thesis Organization

This thesis is organized into five chapters. Chapter 1 provides an introduction of the research, problem statements, objectives and scope of research.

Chapter 2 specifically discusses the theoretical background and the previous literatures study related to the research.

Chapter 3 describes the details of the method used in this research and the work flow of the fabrication and the characterization of Gd-doped ZnO thin films.

Chapter 4 analyzes and discusses the result obtained from the synthesis and the characterization of Gd-doped ZnO thin films.

Last but not least, Chapter 5 summarizes the overall conclusions and recommendation for future works on related topics.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, basic magnetism and ferromagnetism will be explained including the fundamental properties and fabrication method. In addition, rare-earth material will also be discussed in this chapter.

2.2 Principle of Magnetism

Magnetism is a force of nature, which is associated with magnetic field that causes things to attract to each other especially magnetic objects. Magnetic field is like gravitational field where it cannot be seen or touched. The differences between both field are, the gravitational field can be felt, while magnetic field cannot be felt in a direct way. The magnetic field is generated by moving or rotating the electrical charges. From here, it is shown that the magnetic field was existed and the effect can be felt on an object such as magnet, magnetized pieces of metal and etc. For drawing or mapping the magnetic field line, a solenoid was put on a sheet of paper and then the iron fillings were sprinkled on it. Later, the fillings lined up together with the magnetic field and the magnetic field lines that produced by the current in solenoid were shown. Figure 2.1 shows the magnetic field line that produced by current in the solenoid.